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PROCESS DEVELOPMENT FOR SILICON CARBIDE BASED STRUCTURAL CERAMICS

December 1980

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Interim Report for Contract No. DAAG46-80-C-0056

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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A program is underway to develop a process for making shaped silicon carbide base structural ceramics with reduced microstructural flaw size by in situ reaction of silicon with fine, ultra-uniform pored carbon skeletons that are produced from liquid polymer solutions without particulate additions. Thus far, very uniform carbon skeletons in two pore sizes (2.5 and .027 microns) have been produced and siliconized. Very uniform samples of ~1 cm cross section have been produced in a silicon carbide material of ~5 microns average

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ABSTRACT cont

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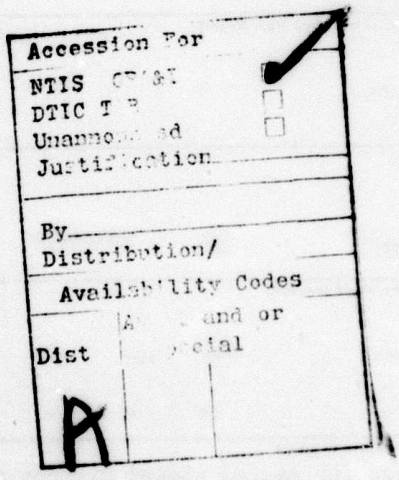

ABSTRACT

A program is underway to develop a process for making shaped silicon carbide base structural ceramics with reduced microstructural flaw size by in situ reaction of silicon with fine, ultra-uniform pored carbon skeletons that are produced from liquid polymer solutions without particulate additions. Thus far, very uniform carbon skeletons in two pore sizes (2.5 and .027 microns) have been produced and siliconized. Very uniform samples of ∿1 cm cross section have been produced in a silicon carbide material of ∿5 microns average size. Limited regions of material with carbide size less than 1 micron have also been produced.

SUMMARY

The overall objective of this research is to develop a process for making shaped silicon carbide based ceramic materials with reduced microstructural flaw size by in situ reaction of silicon with fine, ultra-uniform pored carbon skeletons that are produced from liquid polymer solutions without particulate additions. Subsidiary objectives are: 1) delineation of the maximum section size producible while maintaining microstructural uniformity; 2) production of microstructures with average size reduced from the current level of approximately 5-10 microns to the level of 1 micron or less; 3) characterization of microstructure, corresponding strength levels, and statistical uniformity; 4) delineation of dimensional tolerances and surface finish that can be held during processing without finished machining. Thus far, very uniform carbon skeletons in two pore sizes (2.5 and .027 microns) have been produced and siliconized. Very uniform samples of $\sim$1 cm cross section have been produced in a silicon carbide material of $\sim$5 microns average size. Limited regions of material with carbide grain size less than 1 micron have also been produced. The coarsest of these materials appears to be more uniform and somewhat finer than state-of-the-art materials. In the finest structures produced, the silicon carbide grain size is at least 1 order of magnitude finer than now available. While mechanical properties for the samples thus far produced are not yet available, the microstructural characteristics and uniformity of these materials indicate potentially desirable properties.

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INTRODUCTION

The current search for suitable high temperature structural ceramics has focused on a variety of silicon nitride and silicon carbide based materials. These materials are produced by many methods, including reaction bonding, sintering, hot pressing and chemical vapor deposition. Each process has its advantages, but none has thus far consistently yielded shaped, low cost components with adequate properties to meet the more demanding requirements. Either silicon nitride or silicon carbide appears to have the fundamental bonding required to yield the required combination of:

1) low and high temperature strength and stiffness
2) low coefficient of expansion
3) low density.

Neither material is likely to have enough fracture toughness to use without special designs that acknowledge inherent brittleness and pay special attention to surface conditions. However, modest improvements in fracture toughness can be made through microstructural control. In all the materials thus far available, the full property potential has not yet been realized due to the existance of processing flaws. These flaws are due to: 1) the material's microstructure, and 2) surface finishing or other external load concentrations.

The emerging understanding of failure mechanisms in well designed ceramic parts clearly identifies the maximum flaw size and frequency as performance limiting. The inherently low fracture toughness intensifies the processing requirements, since at the design stresses contemplated the largest tolerable

defect is less than 100 microns which is smaller than readily detectable with current non-destructive evaluation methods. In many of the better materials now available, the strength limiting defects are 30-100 microns, even though these same materials typically possess average microstructural features in the range of 5 microns or less.

In order to fully succeed in the long run, a material and its processing scheme must simultaneously yield:

1) Reproducible, spacially uniform microstructure with minimum flaw size and frequency
2) Low cost-complex-shapes of significant cross section with surfaces requiring little or no finishing.

With the exception of chemical vapor deposition, production of all of the current materials requires the handling of very fine ceramic powder systems. Such powder processing contributes directly to the final microstructural flaw population. The major problems are:

1) Very high surface area, which is often necessary for sintering, leads to excessive agglomeration, surface absorption of impurities, and reaction with high temperature processing atmospheres and causes a multitude of problems including porosity, poor composition control and undesirable residual phases.
2) Very low packing density leads to difficult compaction, tooling wear and contamination, non-uniform density, premature pore closure, porosity, large and

variable shrinkage with concomitant distortions in shaped bodies.

3) High probability of exogenous inclusions arises from the abrasive particles generating foreign particles during all mixing, crushing, grinding, and molding operations. There is no effective means for removal of these particles from the powder mix.

While these problems are routinely handled for many commercial ceramics, the flaw size and frequency and phase control required of high integrity materials demands a new approach.

DEVELOPMENTAL APPROACH

In order to address the objectives and problems outlined above, a significantly different process is under development. In this process no solid particles are incorporated into the body during its formation either as additives or by abrasion during grinding, mixing or molding. The final body is formed by in situ reaction of silicon with a fine and uniform pored carbon skeleton. This is to some extent similar to several commercial methods of producing reaction bonded silicon carbide. However, significant differences are to be noted.

The existing methods all incorporate fine powders in the original body prior to reaction sintering. The carbon reacting to form the final bond of β-silicon carbide is usually a small part of the total carbon in the body. In most cases a substantial

portion of fine α-silicon carbide is mixed with an organic compound, such as a phenolyic resin, that serves as a temporary binder while the body is molded or cast. Often, particles of graphite or other solid carbons are also included with the α-silicon carbide. The organic compound is decomposed leaving the original particles bonded into a porous shaped body whose pore and particle sizes are fundamentally fixed by the original particles and their dispersion during mixing and molding. By adjusting the amount of carbon bond, the average carbon concentration in the body is adjusted slightly below that in silicon carbide, .963 gm/cm^3. However, the local concentration of carbon varies from zero in the pores up to 2.24 gm/cm^3, if graphite is incorporated, over a distance of the order of the agglomerate size of the original particles. In the premium materials, this distance is at least 50 microns and in many cases it is several hundred microns.

The carbon concentration is of vital importance since it determines the local volume change that must take place upon reaction. If the local carbon concentration exceeds that in silicon carbide as it inevitably does in a volume containing only a solid carbon particle, then there must be an expansion when the carbon particle reacts. This expansion is about double if the carbon particle is graphite (2.24 gm/cm^3) rather than disordered carbon which has lower real density ($\sim$1.50 gm/cm^3). A somewhat unusual finding in all the reaction bonded silicon carbide materials is that if the overall carbon concentration in the body is somewhat

less (∿10%) than in silicon carbide, the reaction takes place with negligible overall external dimensional change. This feature is technologically very important since it allows production of close tolerance finished bodies directly from the molded shapes. However, the volume expansion of the reaction must then be taken by expansion into the pores of the body by movement and rearrangement of any solid unreacted particles. The local movement required to achieve uniformity is directly proportional to the scale over which the original body achieved its average carbon concentration. If this size is too large, sufficient accommodation cannot take place and local silicon filled cracks open or some carbon particles are left unreacted.

In both cases a microstructural flaw is left. The ultimate uniformity of the final structure is determined by the uniformity of the original body including its pore size distribution and the size of the original solids as well as their distribution. The flaws present in the commercial materials have been studied in actual components.[1] Instead of the desired structure of fine skeletal silicon carbide interlaced with fine silicon (∿10%), there are regions very high in free silicon, silicon filled cracks, pores, carbon particles and large silicon lakes adjoining large silicon carbide grains.

Sintered silicon carbide has many of the same problems with pores, exogeneous inclusions and occasional very large silicon carbide grains as the major microstructural flaws.

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[1] Reaction of Silicon Carbide with Fused Coal Ash, R. A. Perkins, A. W. Lavendal. E.P.R.I. Report 294 - N.T.I.S. PB-261115, Nov. 1976.

The current process development is a refinement of more than 20 years of experimental work with in situ reactions in porous bodies.[2] There are basically two process areas: 1) production of shaped, controlled porous carbon bodies, and 2) reaction with metallic vapors or liquids. Figure 1 shows the process flow diagram. A previous experimental program[3] has demonstrated that high strength, very reproducible, crack free shaped carbon bodies can be produced with sections greater than 10 cm thick. Fifty molded test strips 5 cm x 2 cm x .125 cm thick were made with a maximum deviation from flatness of .008 cm over their surfaces and a maximum deviation in thickness of .003 cm. These bodies represent a significant advance in uniformity over those previously made. They are spacially very uniform macroscopically and, as well, have the desired carbon concentration over very short distances, ranging from 20 microns in the coarser varieties down to below .1 micron in the finer ones. The carbon concentration can be controlled to within 1% between replicate pieces and between locations on the same piece. The pores are completely intercommunicating and their size distribution is extremely narrow, which facilitates regulation of the subsequent step of reacting the carbon with silicon. The process for producing the carbon skeletons has been previously described.[4] The skeletons of interest in the present program are made from inexpensive,

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[2] U.S. Pat. No. 3,235,346 and 3,348,967, E. E. Hucke, 1966, 1967.

[3] Glassy Carbons, E. E. Hucke, Final Report DARPA, Contract No. DAHC15-71-C-0283, Feb. 1975.

[4] U.S. Pat. No. 3,859,421, E. E. Hucke, 1975.

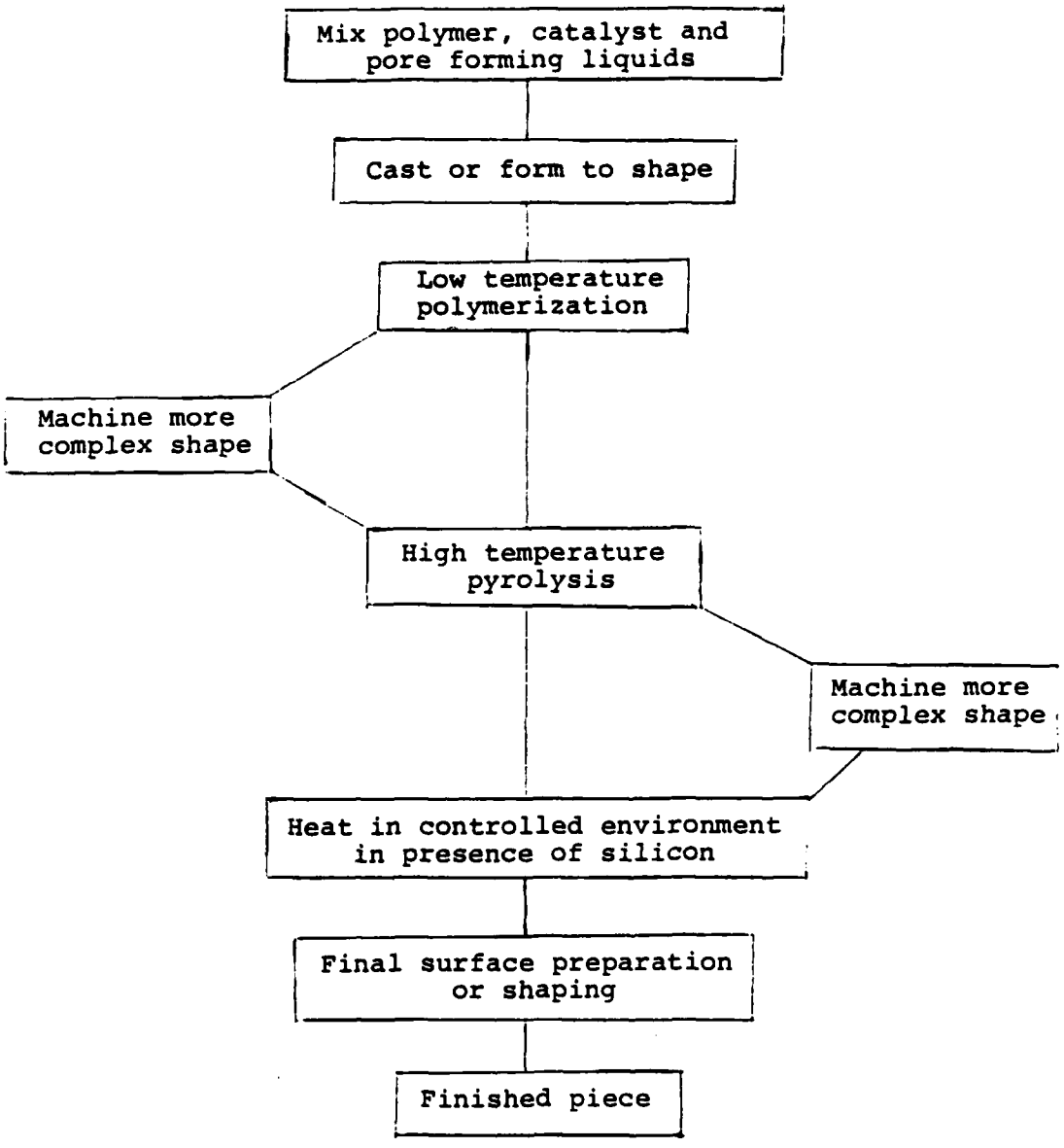


Figure 1. Process Flow Diagram

commercially available liquids, such as furfural alcohol. Simple liquid mixing at ambient conditions with suitable liquid pore formers, dispersants, and catalysts form castable, heat setting polymers. The heat setting or hardening step is typically carried out at temperatures of 100°C or less. The cast and hardened bodies are made up of a continuous polymer network and continuous liquid phase interpenetrating the polymer network. The volume fraction liquid, size and shape of channels are selectable over wide ranges through simple manipulation of liquid types and proportions, catalyst concentration, curing temperature, etc. A controlled pyrolysis in non-oxidizing conditions removes the liquid and converts the polymer network into a controlled porosity isotropic carbon body. The continuous channels left by the liquid allows rapid exit of the gases generated when the polymer is converted to carbon. The body may be further shaped by conventional machining in the polymer state or after carbonization. Pore size can be varied from about 50 Å to 50 microns, while independently controlling the pore volume.

In order to fully exploit the qualities of the carbon skeletons in the subsequent siliconization step, a well controlled reaction is necessary. All reaction bonded ceramic systems release substantial heat causing severe local distortions due to temperature excursions. When solid carbon particles of $\geq$20μ are being reacted, this temperature increase is needed to achieve full reaction since the carbide formed by the reaction tends to limit further reaction. In current materials, this leads to four undesirable microstructural defects:

1) Silicon filled cracks due to local rupture of the body by thermal strain which is especially severe in larger bodies or when large pores rapidly carry liquid silicon deep within the body ahead of the advancing silicon interface.
2) Large grains of silicon carbide. Grain growth is especially severe during the temperature excursions due to solution of the finer carbides and reprecipitation on large particles.
3) Large silicon lakes. The precipitation of dissolved silicon carbide on a few large grains inevitably yields large residual lakes of silicon.
4) Large unreacted carbon particles. When carbon is included in particulate form, inevitably some large particles are present, often by agglomeration of the much smaller original particles. Thus, while the overall carbon content in the body may be at the desired level, the local carbon content is well above that for complete reaction. The silicon available locally is inadequate. This necessarily means that some other volume within the body contains unreacted silicon in excess of that planned. Also, the volume change of the reaction is nonuniform over the sample.

In the present method there are no large carbon particles and the distribution of carbon is uniform over the body. The carbon is no further than a few microns from a continuous pore.

Reaction completely through the carbon is then possible in short times at low temperature. If reactant silicon is supplied at an indiscriminate rate, a large temperature rise occurs as in the usual systems. In fact, the temperature rise would be more severe due to the generally larger surface area in these fine pored skeletons. However, it is possible to control the rate of silicon delivery to the system by controlling the silicon vapor pressure near the surface of the sample. This control may be exercised by direct manipulation of the furnace pressure and temperature. The very fine pored samples (<.1μ) can condense liquid silicon at their surfaces from an atmosphere that is just saturated with a bulk liquid silicon source. The reaction proceeds with either silicon vapor or silicon liquid flowing inward through the very fine uniform pores.

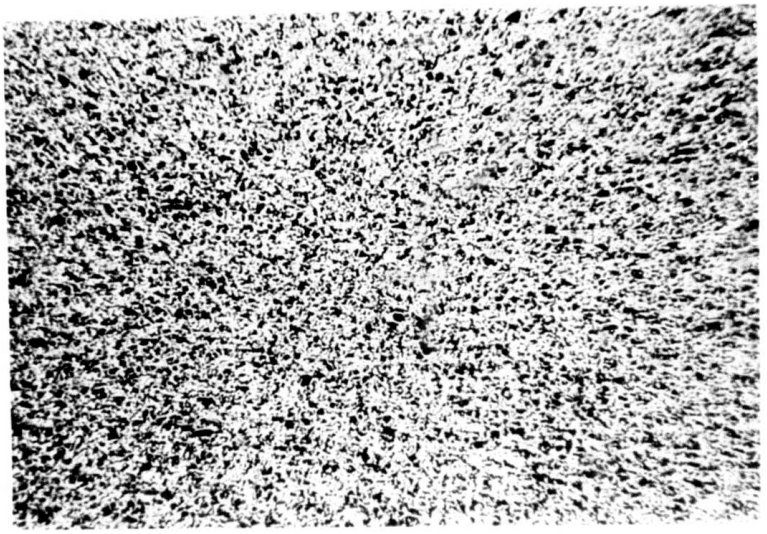
When silicon liquid is supplied at controlled rate to the external surface, the fluid flow can be limited by the very fine pore size of the skeleton. Since the reactant is limited, the heat generated is limited and the reaction can approach isothermal conditions. This condition can lead to complete reaction provided there are no large carbon particles to react. In the special porous carbons this is possible because there are no large pores. In ordinary bodies such control is not possible since a few large pores deliver liquid deep into the sample at very high rates rapidly filling adjacent areas and giving severe thermal spikes.

EXPERIMENTAL RESULTS

Carbon Skeletons

The optimum pore size and particle size within the skeletons must be established by experimental investigation. As a first approximation two carbon skeletons were chosen. The first has a mean pore diameter of about 2.5 microns, while the second is much finer with mean pore size of about .027 microns. It should be noted that even the coarse skeleton is quite fine by usual standards. Glass and silicone rubber molds were prepared for casting the two skeleton types into bar configuration ($\sim$2 cm in diameter x $\sim$15 cm long) and blocks $\sim$15 cm x 15 cm x 5 cm. Approximately ten batches of each skeleton were produced in order to check uniformity between skeleton runs. After casting and hardening the polymer mixtures, carbonization was carried out in a nitrogen atmosphere up to 700°C. All skeletons were subsequently treated for several hours at a temperature of 1750-1800°C under vacuum of $<10^{-3}$ torr and then cooled to room temperature in nitrogen. The target density for skeletons was chosen as .85 g/cm^3, which would theoretically yield a volume percent of silicon after complete reaction of 11.75%. Shrinkage data from the mold dimensions to the finished dimensions were gathered for all skeletons to enable later prediction of the required mold sizes for near net shape castings. Figure 2 shows the typical microstructure of the coarser carbon skeleton.

Macroscopically, a large polished surface showed no indications of cracks or inclusions. The low magnification view in



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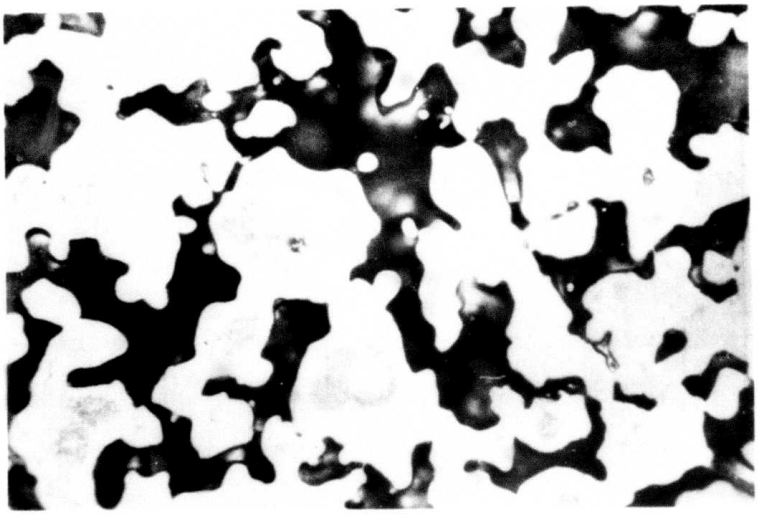

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Figure 2. Typical Microstructure of Coarser Carbon Skeleton.
Top - Low Magnification
Bottom - High Magnification

Figure 2 gives an indication of this uniformity. The 1000X view shows in detail the light area of carbon and the dark area of pore. The average pore size appears to be somewhat greater than 2.5 microns but it should be noted that the pores are elongated and that entrance slits are about 2-5 microns. The largest carbon dimension was found to be ∿20 microns. Assuming the worst case of exi-axed carbon solids, there would then be no carbon further than ∿10 microns from silicon reactant in the pores.

The fine pored skeletons were also macroscopically uniform. At low magnifications, nothing but a highly reflective surface can be seen. Figure 3 shows a high magnification scanning electron micrograph of the fractured surface of a typical fine skeleton. The surface roughness visible appears to be due to the fracture damage as pieces of skeleton were torn free of the surface. This surface roughening is much coarser than the true pore size. Both the coarse and fine skeletons could be polished to a highly reflective surface when observed by the naked eye since in both cases the pore size is relatively fine.

Results of the mercury porosimetry measurements on a typical coarse skeleton are shown in Figures 4 and 5. In Figure 4, the cumulative pore volume versus pore diameter is plotted. It can be seen that there are substantially no pores with entrances coarser than about 4.6 microns and that the bulk of the porosity is in good agreement with the microscopic results. The exceptionally steep rise of the curve indicates the very narrow pore

1 micron ⟵⟶

Figure 3. Typical Microstructure of the Finer Skeleton.

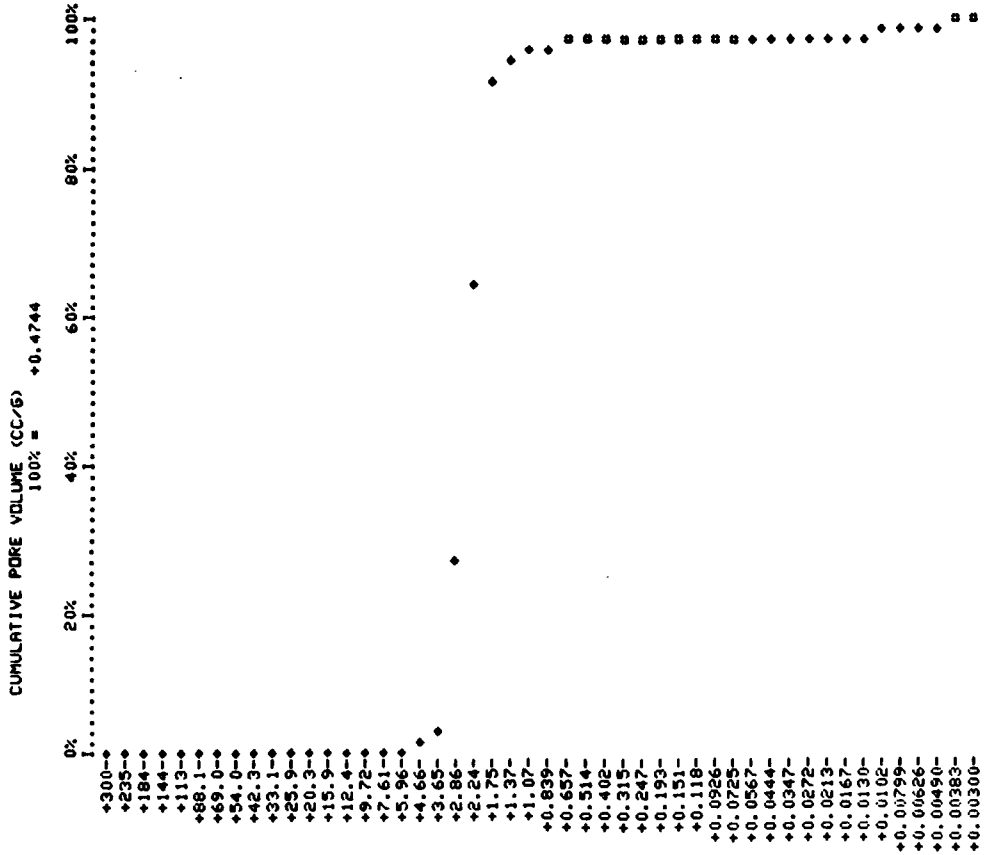


Figure 4. Mercury Intrusion Plot for a Typical Coarse Skeleton.

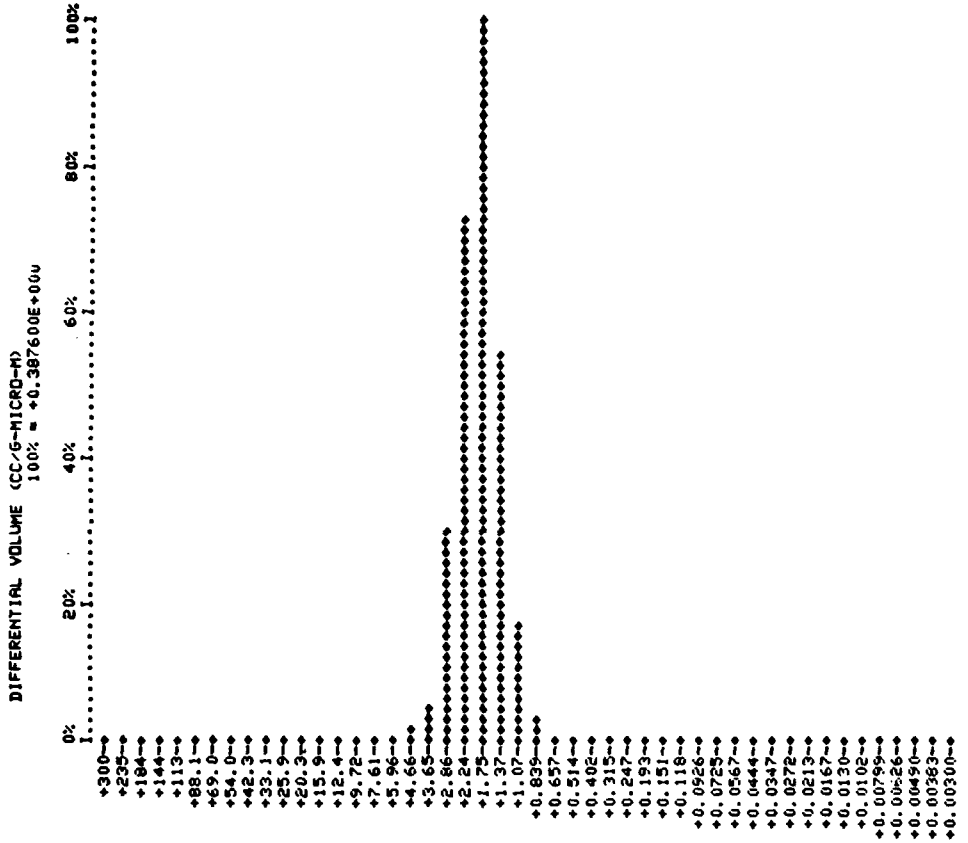


Figure 5. Pore Volume Distribution for a Typical Coarse Skeleton.

size distribution. The real carbon density as determined by mercury intrusion agrees quite well with that measured by absorbing xylene (1.4 to 1.5 gm/cm^3). This finding indicates that virtually all of the porosity within the skeleton is continuous and available to liquids or gases permeating from outside. The mean pore diameter of the sample shown is 2.46 microns. This figure measures the average inlet dimension of the pores. It can be seen from Figure 2 that the largest diameter of the pore is somewhat greater than the narrowest inlet channel. In Figure 5, the differential pore volume is shown versus pore size for the coarse skeleton. This figure dramatically emphasizes the narrowness of the pore size distribution. Virtually the total pore volume lies between one and three microns. The pore surface area of the skeleton as derived from porosimetry is 11.6 sq.m./gm.

Porosimetry results for the fine skeleton are shown in Figures 6 and 7. This skeleton shows no measurable intrusion volume at sizes above .0347 microns. All of the pore volume is available between .01 and .0347 microns. A minor amount of pore volume shown below .00626 microns is probably caused by carbon collapse under the very high pressures needed to force mercury intrusion. Figure 7 emphasizes the narrowness of the size distribution in the fine skeleton. Also in this case real density data indicate that all of the specimen pore volume is accessible from outside the sample. The indicated pore surface area of 90 sq.m./gm is, as expected, higher than for the coarser skeleton.

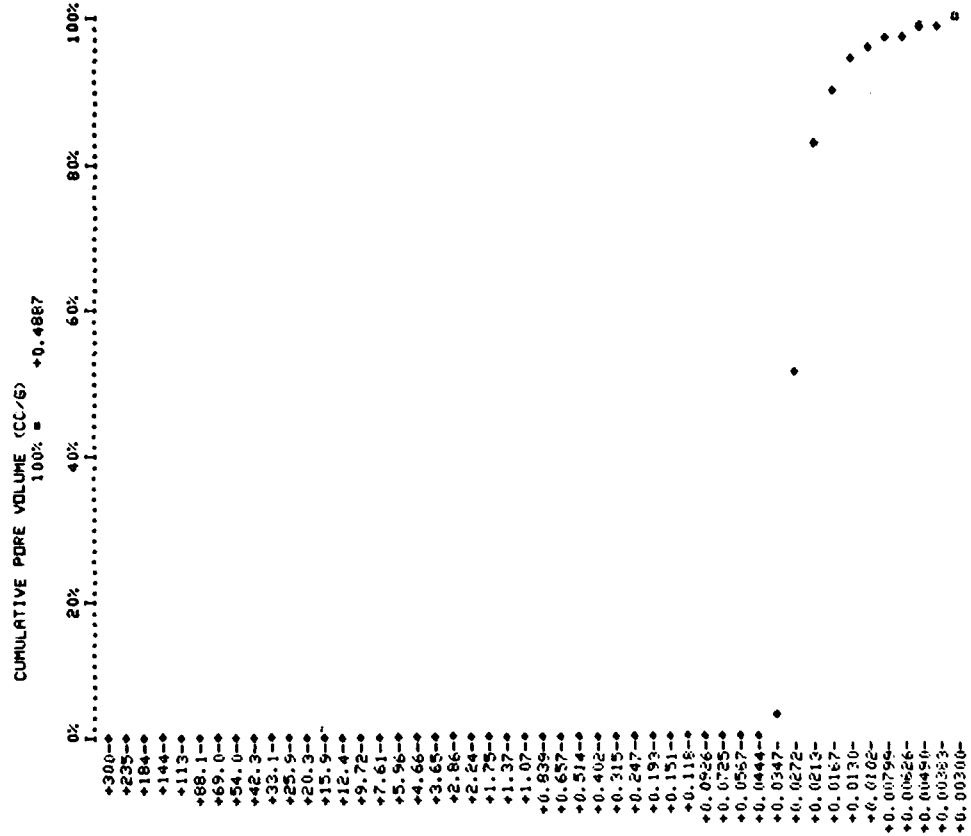


Figure 6. Mercury Intrusion Volume for a Typical Fine Skeleton.

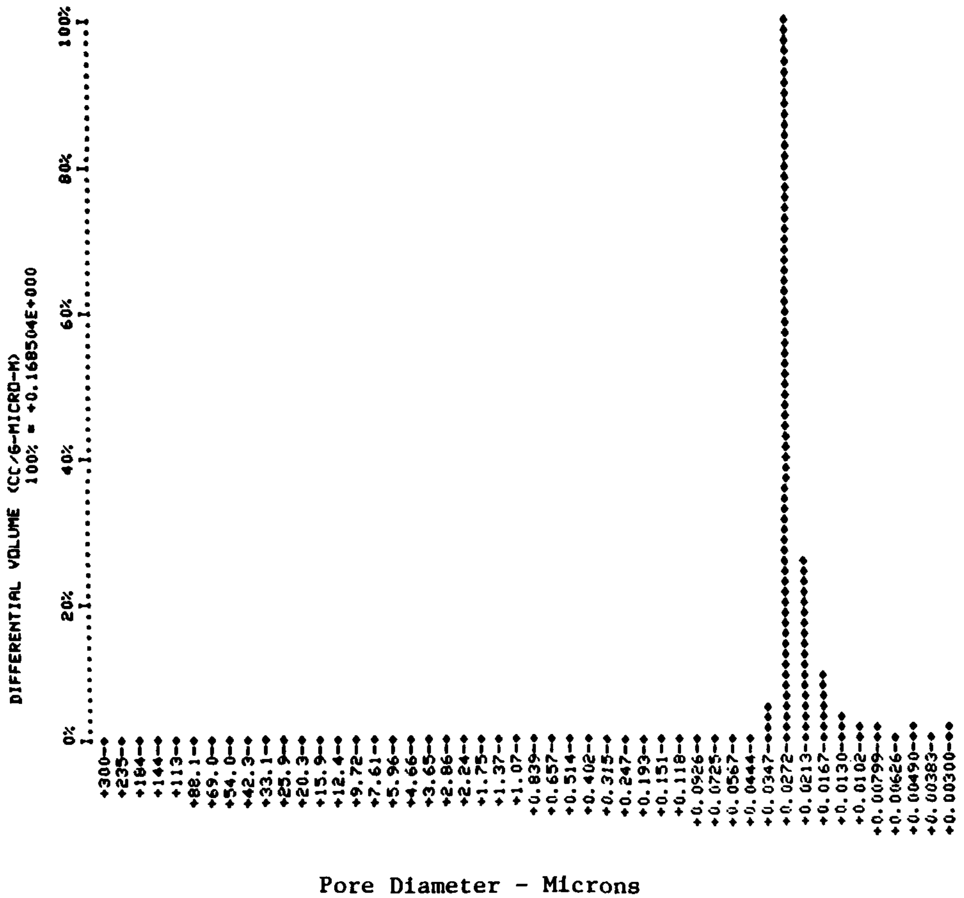


Figure 7. Pore Volume Distribution for a Typical Fine Skeleton.

Reproducibility of skeleton properties was checked on many groups of representative samples. One group of 83 samples was machined from eight different cylinders and the apparent density calculated from measurements and weights. These samples represent various locations within the bar castings. The average density was determined to be .8447 gm/cm^3 with a standard deviation of .0071 gm/cm^3. The standard deviation was found to be approximately the same as that for the average dimensional measurement error. It can therefore be concluded that the spacial density variation is well within 1% and is less than the errors of making simple geometric measurements. The apparent densities determined for replicate batches of the skeletons were found to lie within 1% of the intended values. One anomylous difference was discovered between the density of the cylinders and the large blocks cast from the same polymer mix. The average density for small bars taken from the large casting was approximately 10% less than that from the small cylindrical rods. At present, the reason for this behavior is not understood. Additional experiments are required to fully illuminate this point.

The average linear shrinkage for the skeletons was quite uniform, reproducible, and isotopic. It was 30.5% for the coarser skeletons and 23.7% for the finer skeletons.

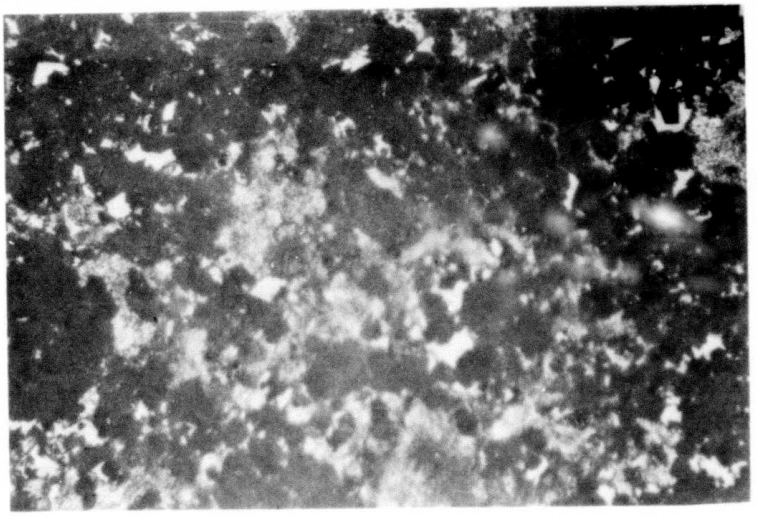
In general, all aspects of the skeleton reproducibility appear to be satisfactory. Quantities of several hundred test bars of two different sizes were machined from the finished carbonized skeletons. The sizes were .638 x .638 x 3.175 cm and .3 x .22 x 4.92 cm. Most of the bars showed good surface finish

and edge retension, but some showed chips and machining marks of sufficient depth to detract from strength. Subsequent work will be done on finishing the bars in the polymer state in order to improve the overall surface finish.

Siliconization

Samples of coarse and fine pored carbon with minimum section size ranging from approximately .2 cm to 1 cm were loaded with silicon into closed graphite containers. The major variables studied were siliconization temperature and exposure time. The material utilized in all experiments was at least 99.9% silicon. After charging, all samples were brought to 1150-1280°C and held under vacuum of less than 10^{-3} torr for several hours. This step was taken to remove gases from the skeleton pores. The furnace chamber was then pressurized with high purity nitrogen to a pressure of between .1 and 20 torr. The chamber temperature was then raised above the melting point of silicon to a chosen temperature between 1450 and 1550°C. The higher siliconization temperatures resulted in complete reactions for all sample and pore sizes. Holding time at the siliconization temperature was varied from a few minutes to over ten hours.

The coarser skeleton gave a duplex grain structure when treated at low temperatures for short time. This same duplex structure could often be noted near the sample external surface, even when the temperature was toward the higher end of the range studied. This structure is illustrated in Figure 8. In this figure, the white areas are silicon while the darker areas are



10 microns

Figure 8. Duplex Structure at the Edge of a Coarse-pored Siliconized Sample.

silicon carbide. In addition, there are extensive regions that are mottled in appearance. These regions are made up of extremely fine silicon carbide with interlaced free silicon. The coarser silicon carbide particles are still fine by usual standards ranging in size from 5 to 10 microns. The silicon carbide in the mottled area is much less than 1 micron in size and very difficult to resolve. Figure 9 shows the structure obtained in the center of the same sample. In this region, the carbide distribution is more uniform and the angular features of the carbide indicates that it was probably precipitated from the liquid upon cooling. In some regions of the coarse skeletons which showed mottled or duplex structure, residual carbon was also noted. Figure 10 shows an example of structure. In this figure the darker areas correspond to the unreacted carbon particles. These structures can be explained in terms of the maximum temperature that the samples probably achieved during reaction. In very small samples, or near the surface of larger samples, or for the lower siliconization temperatures, reaction heat was probably insufficient to locally heat the sample far above the furnace temperature. Such heating causes increased solubility of the carbide in silicon and speeds the dissolution of the fine particles with reprecipitation on the coarse particles. In cases where the reaction exotherm would be smaller, the coarser carbon particles were not completely reacted. It was found through experimentation that these carbon particles could subsequently be completely reacted by holding at siliconization temperatures

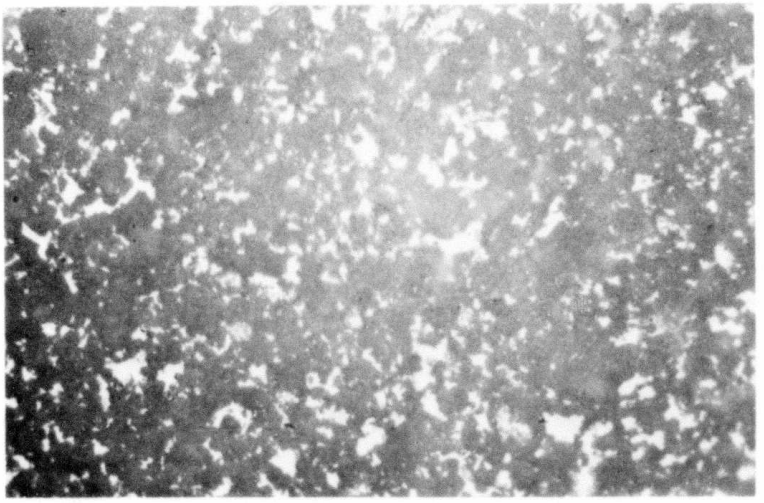


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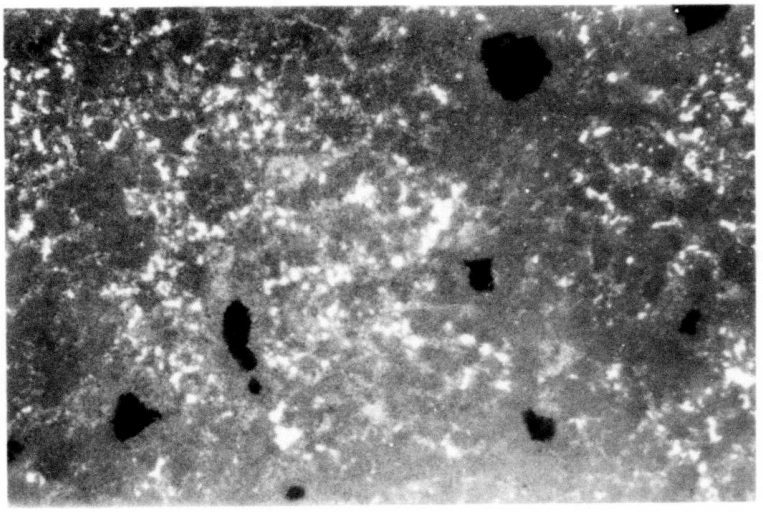
Figure 9. Typical Microstructure at the Center of a Siliconized Coarse-pored Sample.

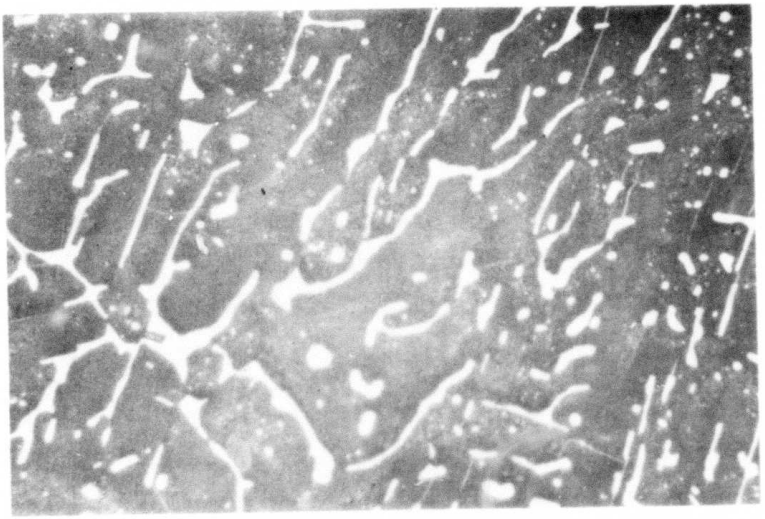


10 microns ⟵⟶

Figure 10. A Region of Duplex Siliconized Coarse-pored Skeleton Showing Residual Carbon as Darkest Areas.

for approximately ten hours. During that time, the areas of fine carbide were coarsened and the structure was that corresponding to Figure 9. It is probable that the reaction heat had fully dissipated in relatively short time and that the prolonged holding period was then sufficient to nearly isothermally react the remaining carbon while causing a minor amount of grain coarsening in the remaining silicon carbide. Siliconization at the higher temperatures probably caused enough reaction heat to be liberated to give a substantial thermal spike resulting in complete reaction and grain coarsening. The structure presumed to be most desirable corresponds to complete reaction of the carbon to very fine silicon carbide with very fine uniform residual silicon completely interpenetrating the carbide. Therefore, future efforts with the coarse skeleton will concentrate on slightly reducing the largest carbon solid dimension within the skeleton so that complete reaction can be obtained at lower temperatures in short times to avoid grain coarsening by solution and reprecipitation.

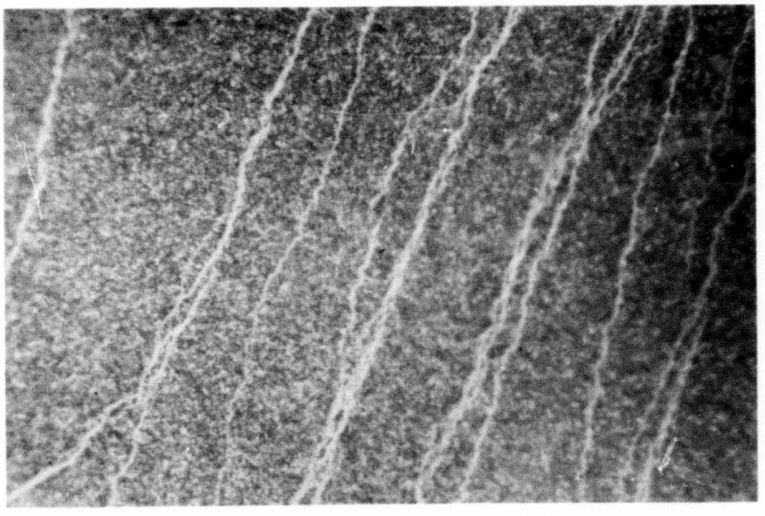
The fine pored carbon skeletons showed a significantly different siliconized structure. These skeletons might be expected to liberate much more reaction heat at constant silicon supply rate. These skeletons yielded two distinctively different structures. The first occurred uniformly throughout the larger samples, especially those treated at higher temperatures. This structure is shown in Figure 11 and consists of very coarse grained silicon carbide with interlaced silicon. It is typical of a structure that has been to a very high temperature and



10 microns ⟵⟶

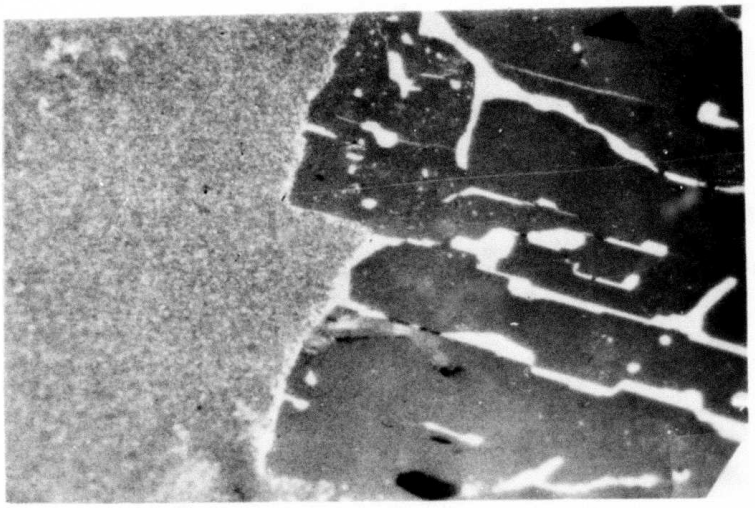
Figure 11. A Typical Siliconized Fine-pored Skeleton that Experienced a Large Reaction Heating.

precipitated large quantities of silicon carbide from the liquid. In these regions the sample was undoubtedly at a much higher temperature than the siliconization chamber temperature. Apparently a very high temperature thermal spike was caused by the reaction exotherm. In other regions, the structure obtained was similar to that shown in Figure 12. There is an extremely fine distribution of silicon carbide that can hardly be resolved at 1000X. The light areas represent the free silicon present. Sometimes there were crack-like rivers of free silicon permeating the fine-grained region. An extreme case of this sort is shown in Figure 12. This structure which should have very good properties was nearly always found in the surface regions of the samples and, in a few exceptional cases, completely across the entire polished section. The crack-like silicon areas are probably caused by the thermal expansion strains of an extreme thermal spike caused when the inner portions of the sample generates heat faster than it can be carried away. If the surface fine-grained regions are ruptured, the silicon is supplied deep within the sample by rapid flow along the rivers giving even more temperature rise. The abruptness of the change in structure is illustrated in Figure 13, where a fine-grained region meets the coarse-grained structure. The coarse-grained structure tended to be located in the center of samples except when the sample was treated at the higher temperatures, making the sample entirely coarse. It appears that the fine-pored skeleton was sufficiently fine to preclude rapid flow into the sample at least during the



10 microns

Figure 12. A Fine-grained Structure in an Outer Region of a Siliconized Fine-grained Sample.



10 microns ⊢—⊣

Figure 13. A Transition Zone Between the Ultra-fined and Coarse-grained Regions of a Siliconized Fine-pored Sample.

early stages of filling or so long as it did not crack. These fine-pored skeletons appear to be just at the limit of the pore size that might be controlled. Further efforts will be made to slightly increase the pore size without introducing coarse carbon particles. It is obvious from the structures studied thus far that the silicon reaction rate in the fine-pored skeletons is sufficient to cause reaction in very short times once the silicon is present since no carbon is more than about 200 Angstroms from a pore. The contrast in structure is remarkable, with the fine dispersion often being <1 micron while the coarse-grained structure is usually >100 microns. Strength properties are not yet available for either of these structures since they have not yet been predictably produced in a given sample.

PROPERTY EVALUATION

Approximately 100 test bar samples of the reacted material were provided to A.M.M.R.C. for preliminary screening of high temperature creep properties. Additional samples are in preparation for room temperature bend strength. A fixture has been built for running 4 point bend tests. A disc rupture testing fixture has been acquired for gathering strength data that is expected to be more reproducible than ordinary 4 point bend tests.[5] Representative samples will be tested and compared with data derived from 4 point bending.

---

[5] Biaxial Flexure Strength of Ceramic Substrates - A Test Method of Uniform Central Loading and Symetrical 3 Point Support, W. Capps. N.B.S. Report CE-4901, 1970.

In addition to the strength data, hardness and fracture toughness derived from hardness testing[6] will be used to routinely compare the properties obtained from various structures. A statistical property set will then be determined after microstructural optimization has taken place.

CONTINUING WORK

Carbon Skeleton

From the results to date, it appears that the two initial skeleton choices span the region of pore and particle size that is most desirable for siliconization. Attempts are to be made to refine the coarse-pored skeleton slightly, particularly with respect to the maximum size of carbon particles. The aim will be to lower this dimension to 2-5 microns. By contrast, the mean pore diameter of the fine skeleton will be increased. Increasing the pore size will substantially reduce the pore surface area which will aid in control of the reaction and help prevent grain coarsening. Attempts will be made to produce a pore diameter of $\sim$.25 microns.

In addition, investigation of machining suitable test bars in the polymer stage is planned. In this way better surface finishes are expected. After standardization of skeleton parameters, molds of simple shapes will be made to test reproducibility of casting carbon parts to near net shape.

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[6]Fracture Toughness Determination by Indentation, Evans and Charles. J. of Am. Ceramic Soc., Vol. 59, 7-8, p. 37.

Siliconization

Further optimization of the siliconization cycles awaits the optimization of the carbon skeleton. Production of a slightly refined coarse skeleton should allow the use of much shorter siliconization cycles at the lowest temperatures. Such cycles should yield much less solution-precipitation growth and yield generally finer structure. Reproducible reaction in the fine-pored structures awaits a reduction in the specific surface area of the skeletons. Since many of the samples produced to date are nearly completely fine-grained across their total section, it appears that relatively minor changes should yield a satisfactory result. Very short siliconization cycles at low temperature should be possible with these modified skeletons.

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APPENDIX "B"

Army Materials and Mechanics Research Center
Watertown, Massachusetts 02172
PROCESS DEVELOPMENT FOR SILICON CARBIDE
BASED STRUCTURAL CERAMICS -
Edward E. Hucke, Materials & Metallurgical
Engineering, The University of Michigan,
Ann Arbor, Michigan 48109

Technical Report AMMRC TR 81-13, December 1980,
38 pp - illus, Contract DAAG46-80-C-0056
Interim Report, 1 June 1980 to 31 December 1980

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Key Words

Silicon Carbide
Reaction Bonded
Silicon Carbide
Structural Ceramics

A program is underway to develop a process for making shaped silicon carbide base structural ceramics with reduced microstructural flaw size by in situ reaction of silicon with fine, ultra-uniform pored carbon skeletons that are produced from liquid polymer solutions without particulate additions. Thus far, very uniform carbon skeletons in two pore sizes (2.5 and .027 microns) have been produced and siliconized. Very uniform samples of ~1 cm cross section have been produced in a silicon carbide material of ~5 microns average size. Limited regions of material with carbide size less than 1 micron have also been produced.

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Figure 4. SAMPLE ABSTRACT CARDS

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